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NO DRAWINGS

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COMPLETE SPECIFICATION

Polyolefine Mixtures free from Melt Fracture

We, CHEMISCHE WERKE HÜLS AKTIEN-GESELLSCHAFT, a German Company, of 4370 Marl, Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

The invention relates to polyolefine mixtures for the production of articles which are free from melt fracture, and which are based either on a low pressure polyethylene, or on a low pressure copolymer of ethylene on the one hand and propylene or butene-1 on the other hand, the low pressure polyethylene having a density of 0.932 to 0.958 g/cc and a reduced specific viscosity of 2.0 to 3.0 measured in decahydronaphthalene at 135°C.

Production of mouldings free from melt fracture is not possible from such polyolefines without further provisions, particularly when they have a narrow molecular weight distribution corresponding to a non-uniformity of 1 to 3. Melt fracture means that the moulding exhibits structures in the form of corrugations consisting of numerous individual indentations in some cases extending over the whole surface. The value of the finished moulding is understably lessened by this.

Attempts are therefore made to remedy this defect as far as possible by variations in the processing conditions (change in the pressure build up, in the temperature programme, in the range of speed of the screw, etc) and also in the mechanical equipment itself (exchange of screws, exchange of tools and the like). Complete avoidance of melt fracture is however achieved only in the rarest cases. An obvious expedient is to influence the rheological behaviour by adding more conventional lubricant, such as stear-

ates, ester salts of polybasic carboxylic acids, paraffin waxes or low molecular weight types of polyethylene and also be various combinations of these groups of substances, to such an extent that a melt fracture can be avoided. Such additions alone are however not successful.

This invention has for its object to provide a mixture which avoids with certainty the serious disadvantage of the said polyolefines.

This object is achieved in accordance with the invention by a content in the polyolefine mixture of 20 to 50% by weight, with reference to the total polymer mixture excluding any additives, of a low pressure polyethylene having a density of 0.935 to 0.950 g/cc, a reduced specific viscosity of 3.2 to 4.8 and a nonuniformity of from 4 to 10.

In another embodiment of the invention the object is achieved by a content in the mixture of 10 to 30% by weight, with reference to the total polymer mixture excluding any additives, of a low pressure polyethylene having a density of 0.935 to 0.950 g/cc, a reduced specific viscosity of 3.2 to 4.8 and a nonuniformity of from 4 to 10, by a content of 10 to 4% by weight with reference to the total monomer components of an apolar rubber which is cross-linkable by sulphur and by a simultaneous addition of 0.1 to 1.0% by weight, with reference to the total monomer components, of a vulcanising agent.

Polyolefines which have a tendency to melt fracture include polyethylenes and copolymers thereof having up to 8% by weight of propylene or butene-1, such as are obtained by special methods, for example by the low pressure method using mixed catalysts of (a) halotitanic esters and (b) trialkyl aluminiums or sesquichlorides, such as form the subject of Belgian Patent Speci-

fication No. 655,813. These polyolefines have outstanding properties apart from the said defect. Polyolefines obtained using catalysts of aluminium silicates containing chromium also have a tendency to melt fracture.

Reduced viscosity η_{red} is calculated according to the formula:

$$\eta_{red} = \frac{1}{c} \times \frac{\eta_L - \eta_0}{\eta_0}$$

where c = concentration (0.1% solution)
 η_L = dynamic viscosity of the solution

η_0 = dynamic viscosity of the solvent.
 A dimension determined with an Ostwald or Ubbelohde viscometer is used for measurement (see Makromol. Chemie 13, (1954), 71). Measurement is in decahydronaphthalene at 135°C.

Nonuniformity is defined as the ratio:

$$\frac{M_w}{M_n} - 1 \text{ where the weight average:}$$

$$M_w = \frac{\sum c_i M_i}{\sum c_i} \text{ is obtained as a good approximation by means of an ultracentrifuge or light scattering, and the numerical average: } M_n = \frac{\sum n_i M_i}{\sum n_i} \text{ is obtained by}$$

means of osmotic measurements (c_i = the concentration by weight having the molecular weight M_i and n_i = the number of molecules having the molecular weight M_i).

The polyethylene to be added to obviate melt fracture is an ethylene homopolymer having a density of 0.935 to 0.950, a reduced specific viscosity of 3.2 to 4.8 and a non-uniformity of from 4 to 10. It is prepared using complex catalyst systems, as for example titanium tetrachloride and an activating organoaluminium compound based on a dialkyl monochloride of aluminium, as for example diisobutyl aluminium monochloride according to Ziegler.

Apolar rubbers are those whose molecular structure is free from heteroatoms, in contrast to polychloroprene rubber or butadiene-acrylonitrile elastomers or also chlorosulphonated polyethylene.

Suitable apolar types which are crosslinkable with sulphur are obtained by various methods, for example by ionic polymerisation or isobutylene and isoprene at -90°C to -100°C by means of aluminium chloride in methylene chloride, so that a butyl rubber is obtained, or by polymerisation of isoprene in cyclohexane by means of a butyl or phenyl lithium catalyst, so that cis-1,4-polyisoprene is obtained; an ethylene-propylene rubber with 0.5 to 10% by weight of dicyclopentadiene prepared using complex

catalyst systems with vanadium chlorides and alkyl aluminiums at -20° to -100°C in tetrachloroethylene (US Patent Specification No. 3,000,866), a cis-1,4-polybutadiene obtained using a catalyst or trialkyl aluminiums and titanium tetrabromides or iodides, or also a butadiene-styrene rubber such as is produced for example by radical chain polymerisation in emulsion using redox systems as for example cumene hydroperoxide and divalent iron ions are also suitable. The agents which may be used for crosslinking include sulphur in the conventional form of flowers of sulphur together with zinc oxide and stearic acid and also if desired other accelerators well-known from the rubber industry, as for example mecapio-benzothiazole, tetramethylthiuram disulphide, di-o-tolylguanidine and the like.

By these additions, the apolar rubbers are firmly incorporated into the molecule as association of the polyethylene components so that a total system results whose meltability is retained.

The moulding material may additionally contain additives conventionally used for thermoplasts, for example antioxidants and stabilisers, such as 4,4'-butylidene-bis-(6-tertiary-butyl-m-cresol), dilauryl thiodipropionate, dibenzylresorcinol and 2-(2'-hydroxy-5-methylphenyl) - benzotriazole, lubricants, such as zinc stearate, sodium stearate, calcium stearate, fatty acid esters and paraffin waxes, antistatics, such as nonylphenylheptethylene glycol, lauryldiethanolamine or coconut fatty acid diethanolamide, pigments of inorganic or organic nature, such as titanium white, cadmium yellow, iron oxide, phthalocyanines and finally also fillers, such as chalk, silicates, sulphates, asbestos, glass fibres and carbon black.

Mixing advantageously begins from the products obtained from the production in powdered form, and these are mixed with the constituents concerned (rubber crumbs, vulcanising agents, antioxidants, lubricants, pigments and fillers) at room temperature and then can be processed into granulate through an extruder with a temperature adjustment between 140° and 210°C, or compaction may take place at the same time as the mixing process by agglomeration at from 100° to 120°C lasting for three to ten minutes in an appropriately heatable mixer. The rubber is thus incorporated into the polyethylene molecular assemblage, probably via sulphur bridges. The use of partly vulcanised or completely vulcanised rubbers does not give the same good results, quite apart from the fact that distribution leaves very much to be desired.

The invention is illustrated by the following Examples.

Example 1

(a) Polymer affected by melt fracture:

The granulate of an ethylene-butylene copolymer containing 0.2 part of 4,4'-thiobis-(6-tertiary-butyl-3-methylphenol) having 4% by weight of butylene, a density of 0.932, a reduced viscosity value of 2.3 and a non-

cylinder (from feed hopper to nozzle):
tool:
nozzle:

uniformity of 2 is extruded as a hose from extruder using a short compression screw (50 D, LD-ratio 15, compression 1:1.7) conventionally used for polyolefines, under the following temperature programme:

140°C, 170°C, 190°C
210°C
200°C

through a nozzle gap of 1 mm and blow moulded into hollow articles having a capacity of 1 litre and a wall thickness of 0.5mm. The extruded hose exhibits a marked melt fracture, and so does the resultant hollow article.

A polyethylene having a density of 0.935 and a reduced specific viscosity value of 2.5 which has been stabilised similarly, behaves in the same way.

(b) Mixture according to the invention:

A mixture of 70 parts by weight of the ethylene-butylene copolymer described under (a) and 30% of an ethylene homopolymer having a density of 0.942, a reduced specific viscosity of 3.9 and a nonuniformity of 8 which has been prepared at room temperature in a high speed mixer is compacted through a granulator and then extruded and blow-moulded to hollow articles under the processing conditions described under (a). Products are thus formed which are entirely free from melt fracture. Even when the short compression screw is replaced by a progressive core screw which is less usual for the processing of polyolefines (50, D, LD-ratio: 15, compression 1:1.7) hollow articles which are free from melt fracture are obtained.

A mixture of the same kind from 50% by weight each of the polyethylene described under (a) and a low pressure polyethylene having a density of 0.936, reduced viscosity value of 3.3 and nonuniformity of 5 behaves similarly.

(c) Mixture according to the invention:

Mixtures of 74% by weight of the copolymers described under (a), 18% by weight of the homopolymers identified under (b) and 7% by weight of a butyl rubber (containing 2.5% by weight of isopropene) having a Mooney viscosity of 45 ± 5 with 0.2% by weight of 4,4-thiobis-(6-tertiary-butyl-m-cresol), 0.07% by weight of sulphur, 0.1% by weight of di-o-tolyl-guanidine, 0.03% by weight of stearic acid, 0.4% by weight of zinc oxide and 0.2% by weight of N-phenyl - N' - isopropyl - p - phenylenediamine is prepared at room temperature, the mixture agglomerated at 115°C for five minutes in a 150-litre mixer and processed as described above into hollow articles. In this case also, mouldings are obtained which are entirely free from melt fracture.

(d) Comparative Example:

A mixture of 70% by weight of the ethylene-butylene copolymer described under (a)

and 30% by weight of an ethylene-propylene copolymer which contains 0.8% by weight of propylene, which has a density of 0.946, a reduced specific viscosity of 3.0 corresponding to a molecular weight of about 130,000 and a nonuniformity of 7, which has been prepared at room temperature in a high speed mixer is compacted through a granulator and extruded under the processing conditions described under (a) and blow moulded into hollow articles. The hollow articles exhibit marked melt fracture.

If an ethylene homopolymer having a density of 0.950, a reduced specific viscosity of 2.7 and a nonuniformity of 8 or the same amount of a corresponding widely distributed ethylene-propylene copolymer having 0.5% by weight of propylene and a reduced specific viscosity of 3.5 be used instead of the ethylene-propylene copolymer, hollow articles having melt fracture are also obtained.

(e) Comparative Example:

When a mixture of 82% by weight of copolymer and 18% by weight of homopolymer or a mixture constituted from 93% by weight of copolymer and 7% by weight of butyl rubber is processed under the conditions of Example (c), the products therefrom exhibit a recognisable melt fracture.

Example 1 therefore makes clearly evident the influence of the reduced specific viscosity of an additional component to an ethylene homopolymer on the melt fracture of a polyethylene at a given wide molecular weight distribution (nonuniformity). It may also be seen that a mixture which, besides the homopolymer of a high molecular weight and wide distribution, also contains a rubber capable of being vulcanised by sulphur, permits a greater participation of starting material affected by melt fracture in the total mixture than is possible than with the sole use of the homopolymer added according to the invention.

The fact that the fundamental behaviour of such mixtures is in no way affected by the simultaneous use of fillers is shown in the following Examples with reference to inactive carbon black fillings, the superiority of the mixtures according to the invention, particularly those containing rubber, again being evident.

Example 2

(a) Comparative Example:

A granulate of 80% by weight of the poly-

- ethylene specified in Example 1(a) and stabilised as described therein, and 20% by weight of an acetylene carbon black having a mean particle size of 43 millimicrons is worked up into tubes having a diameter of 32 mm in an extruder equipped with a tubular tool and a short compression screw (60 D, LD-ratio: 20, compression ratio: 1:3, three zones) first at a speed of the screw of 12 rpm with the following temperature programme (from the feed hopper to the nozzle, including the nozzle, seven heating positions): 135°, 170°, 240°, 250°, 250°, 250°, 260°C. Even at this optimal course of the temperature, tubes free from melt fracture cannot be prepared, and a further increase in the speed of the screw merely causes increased melt fracture so that there is no sense in making tubes from about 25 rpm upwards.

The tubes do not satisfy strength requirements in any way because in creep-stress testing, if they do not burst immediately after applying pressure, they produce random endurance values.

(b) Mixture according to the invention:

- In contrast a mixture which contains, in addition to 80 parts of the mixture from Example 1(b), 20 parts of acetylene carbon black, after previous compaction through a granulator, gives tubes completely free from melt fracture and having a surface resistance of $10^9\Omega$ under the same processing conditions. The speed may be increased in the present case up to the maximum lying at 50 rpm without melt fracture occurring. Considerable technical advantages are associated with the removal of melt fracture. Minimum endurance values of 170 hours and 48 hours are required according to DIN 8075, paragraph 2, requirement A for test stresses of $\sigma = 30$ kp/sq.cm. and $\sigma = 41$ kp/sq. cm. at 80°C; tubes from the mixture according to this invention show the following

ing values, which correspond very well:
 $\sigma = 30$ at 80°C: 953 870 960 960 960 hours
 $\sigma = 41$ at 80°C: 177 225 201 249 169 hours.

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Example 3

(a) Comparative Example:

The granulate of Example 2(a) is processed on the machine of Example 1(a) merely at a cylinder temperature 4°C higher, but otherwise under the same processing conditions, into hollow articles as therein specified.

The hollow articles exhibit marked melt fracture.

(b) Mixture according to the invention:

The granulate of Example 2(b) is processed under the conditions of Example 3(a). Hollow articles are obtained having inner and outer surfaces which are completely smooth and free from melt fracture and having surface resistances of $10^9\Omega$.

(c) Mixture according to the invention:

A mixture is prepared from 20 parts by weight of acetylene carbon black and 80 parts of the mixture from Example 1(c), the butyl rubber merely being replaced by an unsaturated ethylene-propylene rubber having 2.5% by weight of dicyclopentadiene and a Mooney viscosity of 50, the mixture is granulated and worked up according to Example 3(a). Hollow articles are obtained which are completely smooth inside and outside and free from melt fracture and which have a surface resistance of $10^9\Omega$.

For further investigation, the hollow articles from the foregoing Examples are filled to 90% by volume with a mixture of water and glycol in the ratio 1:1 and after having been stored for twenty-four hours at -35°C are subjected at once to a falling test. The height of fall which can be achieved without breakage is compared below for the samples of Example 1:

Sample from Example:—

Height of fall:—

	1(a)	0.5 metre
	1(b)	1.0 metre
	1(c)	1.5 metres
95	1(d)	0.5 metre
	3(a)	0.5 metre
	3(b)	1.0 metre
	3(c)	1.5 metre

- It is surprising that it should be a polyethylene which flows less easily than polymers affected by melt fracture which solves the problem.

- It is also surprising that rubber alone, with or without vulcanising agents and even at dosages which extend far beyond the said upper limit should not obviate melt fracture. It is not obvious to work in the manner claimed, because even an addition of per-

oxide which causes in the order of magnitude of from about 0.005 to 0.01% by weight a lowering of the I_2 value does not obviate melt fracture. It makes no difference whether bis peroxides for example according to US Patent Specification No. 2,916,481 or whether simple mono-peroxides have however been controlled as regards their speed of decomposition by a nitrite addition according to German Printed Appli-

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cation No. 1,127,607 are used for the purpose. Even when otherwise advantageous combinations of substances are used, the result is merely difficulty in processing. Additions of pigments or fillers have no effect on melt fracture.

WHAT WE CLAIM IS:—

1. A polyolefine mixture for the production of articles which are free from melt fracture, and which is based either on a low pressure polyethylene, or on a low pressure copolymer of ethylene on the one hand and propylene or butene-1 on the other hand which contains 20 to 50% by weight, with reference to the total polymer mixture excluding any additives, of a low pressure polyethylene having a density of 0.935 to 0.950 g/cc, a reduced specific viscosity (as hereinbefore defined) of 3.2 to 4.8 and a nonuniformity (as hereinbefore defined) of from 4 to 10.

2. A modified polyolefine mixture as claimed in claim 1 which contains 10 to 30% of the said low pressure polyethylene

together with 10 to 4% by weight with reference to the total monomer components of an apolar rubber capable of being cross-linked by sulphur and 0.1 to 1.0% by weight with reference to the total monomer components of a vulcanising agent.

3. A polyolefine mixture as claimed in claim 1 or 2 which also contains one or more of the following compounds: an antioxidant, a stabiliser, a lubricant, an anti-static, a pigment or a filler.

4. A polyolefine mixture as claimed in claim 1 or 2 substantially as described in Example 1(b), Example 1(c), Example 2(b), Example 3(b) or Example 3(c).

5. Mouldings which have been made from a polyolefine mixture as claimed in any of claims 1 to 4.

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